U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-284 384

Noxious Trace Gases in the Air. Part II Halogenated Pollutants

U.S. Environmental Sciences Research Lab, Research Triangle Park, N.C.

Mar 78

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/J-78-033	2. Journal Article
3. PB 284 384	
4. TITLE AND SUBTITLE NOXIOUS TRACE GASES IN THE AIR Part II. Halogenated Pollutants	5. REPORT DATE
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Philip L. Hanst	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. 1AA603 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

REFERENCE: -Chemistry, 51(2): 6-12, March 1978

16. ABSTRACT

The chemistry of chlorofluorocarbons and other halogenated air pollutants is discussed. A summary is presented of the present levels of concentration of such compounds, along with comments on anticipated increases. Chemical reactions that transform and remove halogenated pollutants in the troposphere are outlined. The penetration of non-reactive pollutants into the stratosphere with resultant destruction of stratospheric ozone is described. Consideration is given to future consequences of continued release of the halogen-containing air pollutants.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Halohydrocarbons * Ozone Nitrogen oxides Hydrocarbons * Photochemical reactions Stratosphere		13B 07C 07B 07E 04A

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 9 22. PRICE A02-A01

EPA Form 2220-1 (9-73)

EPA-600/J-78-033
JOURNAL ARTICLE

Part II. Halogenated Pollutants

Noxious Trace Gases In The Air

Philip L. Hanst, Senior Research Scientist,
Environmental Sciences Research Laboratory,
EPA, Research Triangle Park, NC 27711

Pollution creates ozone in the troposphere, but destroys it in the stratosphere. In an article published last month (3), photochemical smog—a tropospheric phenomenon—was discussed. In this article, the second part of the problem involving man-induced disturbances of the atmospheric ozone is addressed: the reaction of halogenated pollutants with ozone.

While the release of air pollutants containing fluorine, chlorine, bromine, and iodine is rising steadily, concern over effects of these pollutants on human health and welfare is also rising. During the past three years worldwide concern has developed over the possibility that halogenated pollutants may unbalance the natural chemistry of the stratosphere, reducing ozone concentrations, allowing excess ultraviolet radiation to reach the Earth's surface, and changing the planetary climate. Currently halogenated pollutants constitute only a miniscule fraction of the total air pollutant burden (see page 7). A metric ton of air contains only 3 or 4 milligrams of halogenated compounds, but the atmospheric chemistry is such that this small amount of added material might have major consequences.

Concern about halogenated gases in the air began to develop in 1971 when measurements first revealed the accumulation of man-made chlorofluorocarbons. Even though no immediate bad effects of the pollutants had been detected, it was recognized that there might be unforeseen long-range effects. If the removal processes of some halogenated compounds were as extremely slow as suspected, it would take many years for the atmosphere to cleanse itself of certain classes of pollutants.

More specific reasons for concern were based on the physical and chemical properties of the compounds. For example, it has long been known that halogenated gases will readily take up free electrons, forming negative ions. It seems a possibility that such pollutants might alter the ionization properties of the upper atmosphere. Halogenated compounds also have strong infrared absorption bands in wavelength regions in which the atmosphere normally is transparent. It was obvious even in 1971 that halogenated pollutants would change the solar spectrum and might affect atmospheric temperatures and climate.

The major chemical properties of concern involved halogenated compounds' ability to yield highly toxic oxidation products as well as halogen atoms' tendency, in gaseous reactions, to engage readily in chain reactions. Also, there was concern over the carcinogenic properties of halogenated pollutants.

These concerns remain valid. Subsequent research, however, has indicated that the chain reaction property poses the greatest threat to the environment. Potential effects of this property were perceived only dimly in 1971. Since that time it has been established that chlorine atoms released by photodissociation of chlorinated pollutants in the stratosphere can destroy ozone in a long chain reaction.

Families of Halogenated Pollutants

Hydrocarbons may have fluorine, chlorine, bromine, and iodine introduced into their molecular structures in many combinations. In usage, chlorinated compounds predominate by a wide margin, with fluorinated compounds second. Chlorination of methane produces the four basic chemicals: methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform

Reprinted from CHEMISTRY, Vol. 51, March 1978, pp. 6–12
Copyright 1978 by the American Chemical Society and reprinted by permission of the copyright owner

Halogenated compounds

Methyl chloride (CH_3Cl) is the dominant chlorinated hydrocarbon in the air and the only one that is natural in origin. The sea is its most likely source, perhaps as a result of metabolic processes such as vegetative decay.

Dichlorodifluoromethane (CCl_2F_2), also called fluorocarbon-12, is the most abundant of the man-made chlorinated pollutants. The compound is a major threat to the stratospheric ozone balance. Its principal uses are in aerosol propellants and refrigeration applications.

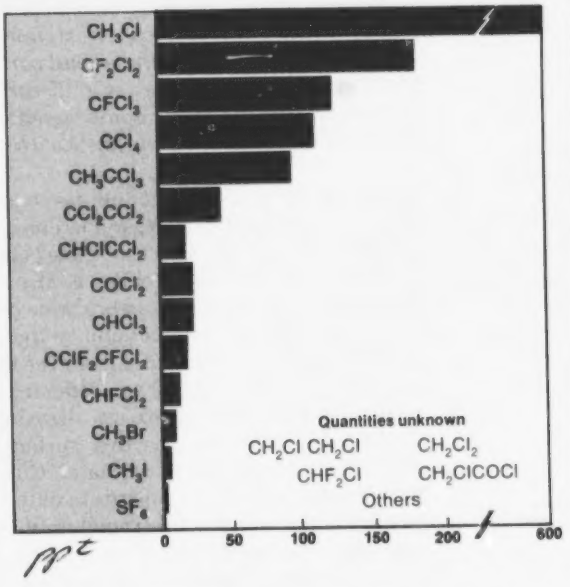
Trichlorofluoromethane (CCl_3F), fluorocarbon-11, is combined with CCl_2F_2 as the propellant in many of the spray products such as hair sprays and deodorants. Since no removal processes have been discovered for fluorocarbon-11 in the troposphere, it must be assumed that stratospheric photodissociation is the outlet for chlorine carried into the atmosphere by this compound. Its chemical behavior, compounded by large tonnage of F-11 releases, have resulted in F-11's rank as a major threat to the stratospheric ozone balance.

Carbon tetrachloride (CCl_4) appears to be a principal chlorine carrier, migrating to the stratosphere and interacting with the ozone. The present annual release of carbon tetrachloride pollution, however, is small compared to the annual releases of some of the other chlorinated compounds. Because of health hazards, home uses have been severely curtailed and venting of CCl_4 to the atmosphere occurs mainly during industrial operations such as the production of fluorocarbons.

Methyl chloroform (CH_3CCl_3) is used heavily in metal cleaning and degreasing, and as a dry-cleaning solvent. Methyl chloroform is resistant to oxidation, having a tropospheric lifetime of about 10 years. Thus a portion of the methyl chloroform pollution will find its way into the stratosphere where the chlorine atoms will be released by photolysis to attack ozone.

Perchloroethylene (C_2Cl_4) is used mainly in dry cleaning. The emissions are large, but the atmospheric lifetime of the compound is short—probably on the order of several weeks. Little is known of the fate of the photooxidation products. The main product is trichloro acetyl chloride, and a lesser product is phosgene.

Trichloroethylene (C_2HCl_3) is produced in the photooxidation of many types of halogenated pollutants, including four of the six mentioned above. The phosgene is undoubtedly removed in precipitation, but its rate of removal is slow enough to allow a background concentration of about 30 ppt to remain in the tropospheric air.



Small amounts of chloroform ($CHCl_3$) are mixed throughout the troposphere. At present it is not clear whether this is a man-made pollutant or a natural pollutant.

The figure shows several of the other compounds that have been seen in the air remote from sources—fluorocarbon-113 ($C_2Cl_3F_3$), fluorocarbon-22 ($CHFCl_2$), methyl bromide, methyl iodide, and sulfur hexafluoride.

Compounds expected to be present but not yet detected include dichloroethane, chlorinated acetyl chlorides, and other halogenated products of atmospheric reactions.

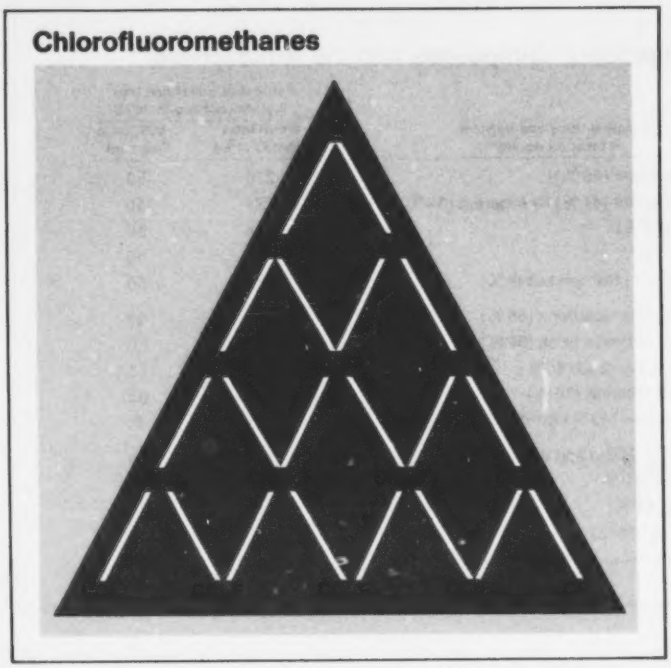


Figure 1. The family of chlorofluoromethanes includes some major commercial fluorocarbons as well as basic methane derivatives

($CHCl_3$), and carbon tetrachloride (CCl_4). When combinations with fluorine are considered, 13 methane derivatives are possible (Figure 1). This family of *chlorofluoromethanes* includes the major commercial fluorocarbons F-11 (CCl_3F), F-12 (CCl_2F_2), F-21 ($CHCl_2F$), and F-22 ($CHClF_2$). When bromine and iodine substituents are considered, the family becomes much larger.

If the chlorine- and fluorine-substituted *ethanes* are also considered, a dramatic increase in family size takes place. The number of chlorofluoroethanes is in the fifties, including several compounds of major commercial importance—methyl chloroform (CH_3CCl_3), ethylene dichloride (CH_2ClCH_2Cl), fluorocarbon 113 ($C_2Cl_3F_3$), and fluorocarbon 114 ($C_2Cl_2F_4$). When bromine and iodine substituents are added, the family of halogenated ethanes becomes extremely large.

The third major family of halocarbons is the substituted *ethylenes*. In this family only the chlorinated members, which include vinyl chloride (C_2H_3Cl), vinylidene chloride ($C_2H_2Cl_2$), trichloroethylene (C_2HCl_3), and perchlorethylene (C_2Cl_4), currently have major commercial importance.

Chlorofluorocarbon names are based on a three-digit number, XYZ. Z represents the number of fluorine atoms in the molecule, while Y is the number of hydrogen atoms in the molecule plus one. X, the number of carbon atoms minus one, is omitted if it is zero

World-Wide Emission of Halocarbon Pollutants

Although many halocarbons are known, only a few are released to the atmosphere in major quantities; some of these are removed quickly by oxidation but others remain and accumulate. In the cases of ethylene dichloride, vinyl chloride, carbon tetrachloride, methyl chloride, ethyl chloride, and chloroform, large amounts are produced but are then converted to other compounds. There is some emission into the air, however, due to losses in handling. Other compounds are basically produced for disposal in the atmosphere, so production and eventual release of pollutants are equal (Table I).

Fifty percent of present world-wide production and emission of halocarbons comes from the United States, 35% from Europe, and 15% from the rest of the world. Emissions for 1973 consisted of 20% fluorocarbons and 80% other chlorinated pollutants. Most of the 80% nonfluorocarbon portion is transformed to other chlorinated compounds in the troposphere and lower stratosphere. It is necessary, therefore, to examine the transformation chemistry and identify the pathways for removal of halogens from the atmosphere.

Measurement Methods

To understand man-induced disturbances of the atmosphere, one must measure the disturbing materials. Measurement of gases at concentrations smaller than one part-per-billion requires the greatest possible extension of air analysis techniques. The two principal measurement methods in current use are gas chromatography and infrared spectroscopy. The gas chromatographic method is usually applied to air samples that are captured and returned to the laboratory and the infrared method is mainly applied to the undisturbed atmosphere. Progress in determining the fate of halogenated pollutants and their effects in the environment will be accelerated by further improvement of these measurement methods.

Transformation of Halocarbons in the Air

Some compounds have high emission rates but react fast and appear in the ambient air only at low concentrations. Products of the reactions, however, may persist in the air longer than the parent compounds and also may be more toxic. Prominent members of this class are perchloroethylene, trichloroethylene, methylene chloride, and chloroform. The tropospheric chemistry of these compounds must be fully understood before their environmental impact can be assessed. Other compounds such as carbon tetrachloride, fluorocarbon-11, and fluorocarbon-12 react very slowly and can accumulate in the air. These may become major halogenated pollutants even though their rates of emission are relatively small. In the absence of rapid removal processes in the troposphere, stratospheric removal takes over.

All compounds diffuse upward into the

Table I. Estimated Emissions of Halogenated Compounds into the Atmosphere

Compound	World production in 1973, millions of kg	Principal uses and percent of total production	Estimated emissions into the atmosphere in 1973	
			World total, millions of kg	U.S. total percent
Fluorocarbon-11	302	Aerosol propellant (78%)	270	50
Fluorocarbon-12	441	Aerosol propellant (47%) Refrigerant (34%)	333	50
Fluorocarbon-22	122	Refrigerant (66%)	54	50
Fluorocarbon-113	50	Solvent (85%)	45	50
Fluorocarbon-114	45	Propellant (91%) Refrigerant (9%)	32	50
Carbon tetrachloride	941	Production of fluorocarbons (88%)	40	50
Chloroform	224	Production of fluorocarbons (90%)	5	50
Ethyl chloride	545	Produce tetraethyl lead (85%)	13	55
Ethylene dichloride	11880	Produce vinyl chloride (78%)	563	35
Methyl chloride	396	Produce silicones (43%) & tetramethyl lead (38%)	5	60
Methyl chloroform	405	Metal cleaning (70%) and degreasing	376	60
Methylene chloride	421	Paint remover (40%)	342	55
Perchloroethylene	743	Dry cleaning (65%)	617	45
Trichloroethylene	693	Metal cleaning (86%)	626	30
Vinyl chloride	7020	Produce polyvinyl chloride (89%)	348	25

stratosphere and eventually are destroyed by ultraviolet photodissociation. The molecular fragments then react with ozone, oxygen, methane, and other compounds in the stratosphere until stable final products are reached. These products eventually diffuse downward to be removed by tropospheric precipitation. It is during the break-up and removal processes that halogen atoms engage in chain reactions that destroy stratospheric ozone.

Methyl chloroform, fluorocarbon-22, and fluorocarbon-21 are pollutants of intermediate reactivity that partially penetrate the stratosphere. These compounds are removed through a combination of slow photochemistry and photodissociation involving both tropospheric and stratospheric chemistry.

Tropospheric Chemistry

Hydroxyl radicals are the principal attacking species in the troposphere and, in the case of substituted paraffins, hydrogen abstraction is the initial reaction. A typical case is the attack on chloroform.

$$OH + CCl_3H \rightarrow H_2O + CCl_3$$

The free radical CCl_3 then reacts with oxygen to yield phosgene and ClO.

$$CCl_3 + O_2 \rightarrow COCl_2 + ClO$$

The phosgene will remain intact until it is either washed out or photodissociated. The rate of washout has not yet been determined. If it is extremely slow, the major part of the phosgene will migrate upward and be photodissociated in the lower stratosphere. If the washout is fast, the impact of the phosgene on the stratosphere will be slight.

The ClO will oxidize another molecule and yield Cl atoms. In the troposphere, NO and HO_2 are candidates for reaction.

$$ClO + NO \rightarrow Cl + NO_2$$

$$ClO + HO_2 \rightarrow Cl + OH + O_2$$

Most Cl atoms react quickly with methane.

$$Cl + CH_4 \rightarrow HCl + CH_3$$

Similar reaction schemes exist for each of the halogenated paraffins having one or more hydrogen atoms in the molecule. Other products in addition to phosgene include acetyl chloride, chlorinated acetyl chlorides, and homologous molecules in which fluorine is substituted for one or more chlorines.

In the case of chlorinated ethylenes such as perchloroethylene, the attacking OH radical opens the double bond, allowing oxygen to enter. By a mechanism that is not yet understood, the perchloroethylene is then converted to trichloro acetyl chloride.

$$C_2Cl_4 + [O] \rightarrow CCl_3COCl$$

The rates of hydrolysis and washout of this product have not yet been measured.

Stratospheric Chemistry

The portion of halogenated pollution that reaches the stratosphere—including all of the fully halogenated compounds—is broken down by the attack of energetic photons. For example, in carbon tetrachloride the absorption of a photon removes a chlorine.

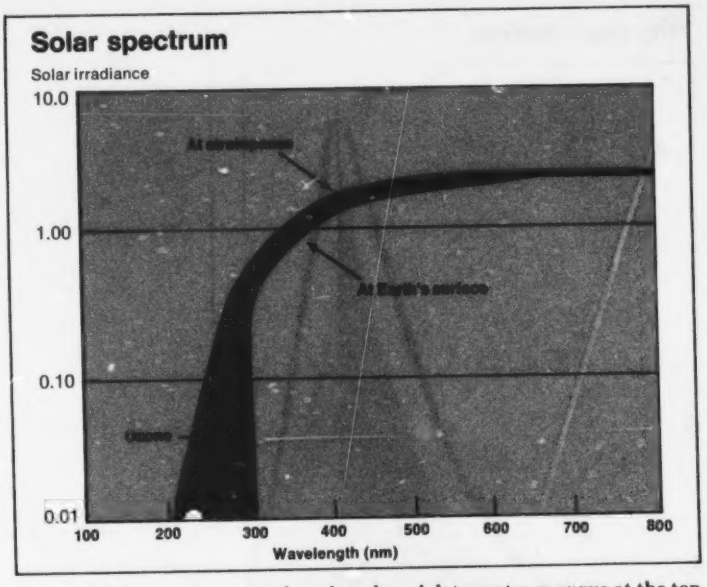


Figure 2. The area between the solar ultraviolet spectrum curve at the top of the stratosphere and at the Earth's surface represents radiation absorbed by ozone in the atmosphere. Solar irradiance is measured in number of photons (10^{15}) of specific wavelength (5 nm) that strike a given cm^2 every second

$$CCl_4 + h\nu \rightarrow CCl_3 + Cl$$

The CCl_3 radical is oxidized to phosgene just as in the case of chloroform in the troposphere. But in the stratosphere, the resultant Cl atoms and ClO molecules do not go directly to HCl. Instead, they react most readily with the "odd oxygen"—ozone and oxygen atoms. This is the beginning of the chain reaction. Starting with the chlorine atom, the first reaction of the cycle is ozone destruction.

$$Cl + O_3 \rightarrow ClO + O_2$$

Because ozone is constantly being photodissociated, there are also oxygen atoms present which react with ClO.

$$O_3 + h\nu \rightarrow O_2 + O$$

$$O + ClO \rightarrow Cl + O_2$$

After two ozone molecules have been removed from the scene, the chlorine atom is ready for two more. This cycle will continue until the chlorine atom reacts with methane or some other hydrogen-containing species and becomes tied up in hydrogen chloride.

$$Cl + CH_4 \rightarrow HCl + CH_3$$

The hydrogen chloride will migrate downward, but it will not hold the chlorine permanently. An OH radical will get to the HCl before it has moved very far and remove the hydrogen.

$$OH + HCl \rightarrow H_2O + Cl$$

The Cl is now free to engage again in the ozone destruction chain. This removal and return of the Cl to the chain will happen ten or more times before the Cl can diffuse out of the stratosphere. The total number of ozone molecules destroyed by one chlorine atom can run into the thousands. Eventually, however, the hydrogen chloride reaches the troposphere and is washed out in rain.

In 1974, M. J. Molina and F. S. Rowland of the University of California predicted that the increasing use of chlorofluorocarbons as aerosol propellants, foaming agents, and refrigerants could seriously deplete the stratospheric ozone. Subsequent studies by many research groups have led to predictions of depletion between 2 and 20%. These studies are summarized in reports by the National Academy of Sciences (*7*, *8*) and the National Aeronautics and Space Administration (*6*).

Effects of Stratospheric Ozone Reduction

Stratospheric ozone is the chief absorber of solar ultraviolet radiation, providing a protective shield against radiation damage to living things. Figure 2 shows the solar ultraviolet spectrum at the top of the stratosphere and at the Earth's surface. The area between the two curves corresponds to the radiation absorbed by the atmosphere. Stratospheric ozone contributes all of the absorption except for the small oxygen contribution represented by the bump at the bottom of the figure.

If stratospheric ozone lessens, the spectral curve at the Earth's surface will move toward shorter wavelengths. The increased radiation will then cause an increase in human skin cancer. There will be nonhuman biological effects as well. The sensitivity of living things to ultraviolet rays increases strongly as wavelength decreases. A recent report on halocarbons issued by the National Academy of Sciences (*8*) shows the relationship in terms of the effectiveness of a quantum of light in altering DNA, the genetic code molecule of all living things, as follows:

Wavelength	Degree of DNA Damage
320 nm	0.03
310 nm	0.60
300 nm	15.00
290 nm	160.00

Clearly, any change of the solar spectrum in the critical region around 300 nm is to be viewed as a grave threat to the biosphere.

The second major reason for concern over ozone loss is the possible effect on climate. As the distribution of energy-absorbing molecules changes, the temperature distribution will change. Changes in weather and climate will

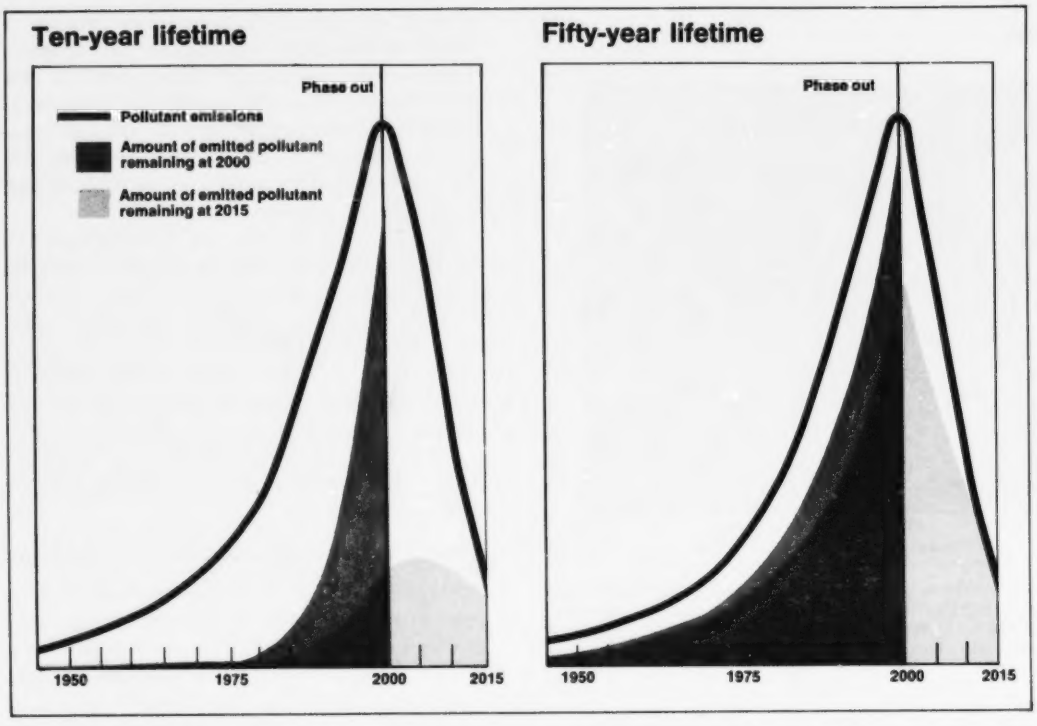


Figure 3. The emissions of the pollutants with a 10-year lifetime and a 50-year lifetime are shown by the area under the black curves. Emissions increase 6% each year between 1945 and 2000, followed by a phase-out between 2000 and 2015. The total accumulations by the year 2000 are shown by the areas under the green curve. The total accumulations of the pollutants by the year 2015 are indicated by the total area under the gray curve. After 2015, the short-lived compound decays five times faster than the other.

result. There is little doubt on the basic point, but there is great uncertainty as to the magnitude of the changes. If atmospheric temperature changes due to halogenated pollutants would never exceed more than a small fraction of one degree, the weather and climate effects would be negligible. Unfortunately, no such assurance of small temperature change can be given. The prediction of weather and climate changes seems to be at the end of a progression of uncertainties. One starts with the prediction of halocarbon pollutant accumulations; there is only a moderate degree of uncertainty here. Next comes the prediction of ozone depletion and other chemical effects from the accumulated halocarbons. In this prediction the uncertainty has increased. Next are the difficult predictions of temperature change due to changes of radiation absorption and emission. Finally there is the ill-defined connection between atmospheric temperature patterns, weather, and climate.

Relationship Between Pollutant Lifetime and Atmospheric Restoration Time

The attack on stratospheric ozone by halogenated pollutants is only in its beginning phases. Actually, it has not been shown that there is any change in ozone layer thickness due to halogenated pollutants. One may well ask, then, why there should be such great concern and intense interest in the halogen–ozone interactions. The answer lies in the long lifetime of the fully halogenated pollutants. Compounds like CCl_4, CCl_3F, and CCl_2F_2 are removed only in the stratosphere, where the destruction of ozone is an unavoidable byproduct of removal. Since the troposphere contains about ten times more air than the stratosphere, the transport of the pollutants into the stratosphere would continue for many years after the release of pollutants was stopped.

These factors combine to give the fully halogenated compounds an atmospheric lifetime of about 50 years. The reduction in pollutant concentration after emissions ceased would, in fact, be an exponential function, with 50 years being the time for the concentration to fall to 37% of its starting value. For those pollutants with a tropospheric removal process, such as attack by OH radicals, the lifetimes are relatively short. For example, the lifetime of perchloroethylene is measured in months. On the other hand, for methyl chloroform, in spite of the presence of three hydrogen atoms in the molecule, the lifetime may be 10 years.

Figure 3 shows the accumulation of two pollutants, one with a 10-year lifetime and the other with a 50-year lifetime. Accumulations are compared for a case in which the emissions increase 6% per year between 1945 and 2000 followed by a phase-out of emissions between 2000 and 2015. Total emissions are indicated by the total area under the black curves. Accumulations of the pollutants between 1945 and 2000 are shown by the areas under the green curves. The area under the green curve for the compound with a 50-year lifetime is about double that of the other compound at the year 2000. Similarly, the areas under the gray curves show that at 2015 the amount of the 50-year-lifetime pollutant would be about four times as great as the amount remaining of the 10-year-lifetime compound. Thereafter, the shorter-lived compound would decay five times faster than the longer-lived compound.

Brominated Compounds

Because the removal of bromine by methane is slow, a bromine atom in the stratosphere may be more damaging to ozone than a chlorine atom. Ethylene dibromide ($C_2H_4Br_2$) is by far the largest commercially produced bromine-containing compound, with use as a gasoline additive and as a soil and grain fumigant. In the 1960s, world production of ethylene dibromide was about 110 million kilograms per year. Bromine in the gasoline mostly ends up in lead salts which are washed into the ground, but the influence of ethylene dibromide on the stratosphere is probably negligible.

Methyl bromide (CH_3Br) is the second principal brominated pollutant. It is mainly used for fumigation of soils and stored commodities to kill rodent and insect pests. Methyl bromide is more expensive than ethylene dibromide, and therefore is used on a smaller scale, but much of this methyl bromide undoubtedly ends up in the atmosphere. Some methyl bromide seems to be released in nature along with the methyl chloride; this matter needs to be investigated further.

Bromotrifluoro methane ($CBrF_3$) is also of interest because of its use in fire extinguishers. Since this is a fully halogenated compound, it can be expected to have a lifetime long enough for the bromine to be transported to the stratosphere. The lifetime of the compound and the action of the bromine atoms in the stratosphere are currently under study.

What Can and Should Be Done?

There are two kinds of actions that should be taken. The first, to seek answers to the remaining questions about the transport and reactions of the halogenated pollutants. The second is to begin to restrict the nonessential uses of fully halogenated pollutants. The continuing research program must address such questions as: What are the concentrations of OH radicals in the atmosphere and how do they vary with time, latitude, and altitude? To what degree is stratospheric chlorine tied up in forms other than hydrogen chloride—such as in chlorine nitrate and hypochlorous acid? What are the atmospheric lifetimes of phosgene and the acetyl chlorides? Is a brominated pollutant a greater threat than a chlorinated pollutant? How toxic to humans are small concentrations of the halogenated reaction products formed in the air from the halocarbons?

Restrictions on the uses of fully halogenated pollutants are already being planned. In May 1977, three U.S. government agencies—the Food and Drug Administration, the Environmental Protection Agency, and the Consumer Products Safety Commission—proposed a timetable for the phasing out of *nonessential* uses of fluorocarbons. The classification as nonessential will rest largely on whether there is an acceptable alternative to usage. In the cases of deodorant sprays and hair sprays, for example, there are many acceptable alternatives to the use of fluorocarbon propellants. But some medical uses, as in asthma-treatment sprays, are judged to be beneficial enough that they will not be phased out at present. In the cases of air conditioning and refrigeration, the development of feasible alternatives will take time and the phasing out of these uses is also being deferred. Action by the U.S. government can substantially reduce the threat to stratospheric ozone, but the global nature of the problem calls for international action.

Suggested Reading

(1) Crutzen, P. J., "A Review of Upper Atmosphere Photochemistry," *Can. J. Chemistry*, **528**, 1569 (1974).
(2) Hanst, P. L., "Spectroscopic Methods for Air Pollution Measurement" in "Advances in Environmental Science and Technology," Vol. 2, J. N. Pitts, R. L. Metcalf, eds., John Wiley and Sons, Inc., NY, 1971.
(3) Hanst, P. L., "Noxious Trace Gases in the Air, Part I. Photochemical Smog," *Chemistry*, **51** (1), 8–15 (1978).
(4) Rowland, F. S., Molina, M. J., "Chlorofluoromethanes in the Environment," *Rev. Geophys. Space Phys.*, **13**, 1–36 (1975).
(5) Williams, W. J., Kosters, J. J., Goldman, A., Murray, D. G., "Measurements of Stratospheric Halocarbon Distributions using Infrared Techniques," *Geophys. Res. Let.*, **3**, 379 (1976).
(6) "Chlorofluoromethanes and the Stratosphere," National Aeronautics and Space Administration, Ref. Pub. 1010, August 1977.
(7) "Halocarbons: Effects on Stratospheric Ozone," National Academy of Sciences, 1976, Printing and Publishing Office, 2101 Constitution Ave., NW, Washington, DC.
(8) "Halocarbons: Environmental Effects of Chlorofluoromethane Release," National Academy of Sciences, 1976, Printing and Publishing Office, 2101 Constitution Ave., NW, Washington, DC.